

Relating Ocean Optics to Photochemical Transformations of Dissolved Organic Carbon In Coastal Waters

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LONG-TERM GOAL

The long-term goal of this research is to use remotely sensed ocean optical data for estimates of the regional and global scale significance of photochemistry to dissolved organic carbon (DOC) cycles and optical changes resulting from these processes.

SCIENTIFIC OBJECTIVES

The central objective of this research program is to examine quantitatively the links between optical measurements and photochemical carbon transformations in the sea. Our goal is to establish quantitative methods to relate variability in water-leaving radiance to photochemical reactions that lead to direct loss of colored dissolved organic matter (CDOM) and consequent changes in UV optical properties in the photic zone. By examining these quantitative relationships, we also hope to gain both an understanding of the dominant variables controlling UV optics in the mixed layer and the critical parameters influencing DOC photochemical reactions in seawater.

APPROACH

To achieve the objectives stated above requires a wavelength dependent description of the *in situ* optical field for ultraviolet radiation (UV) together with spectral efficiency data for photooxidation of CDOM. Our general approach uses three connected principles:

- (1) Diffuse attenuation coefficients for visible spectral irradiance can be related to ocean color (i.e., ratios of near-surface water-leaving radiance; Austin and Petzold 1981). Our results thus far indicate that comparable relationships between water-leaving radiance in the visible and diffuse attenuation of UV radiation can also be determined.
- (2) CDOM is a dominant contributor to the absorption and attenuation of UV in coastal waters. With appropriate caution, and proper accounting for adsorption by particles, diffuse attenuation of UV can be related directly to absorption by dissolved organic matter.
- (3) The absorption of UV by CDOM leads to photochemical transformations that include the destruction of chromophores and the production of lower-molecular weight compounds. Wavelength-dependent quantum yields for these transformations can be determined experimentally as action spectra.

Given measurements of solar radiation and upwelling radiance at the sea-surface, we will estimate

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photochemical transformations of surface-layer DOM by applying empirical relationships between: (1) reflectance and diffuse attenuation, (2) spectral diffuse attenuation and UV absorbance, and (3) UV absorbance and action spectra for photochemical transformations.

Field optical data are collected with two instruments (Satlantic, Inc.) that add UV measurements to visible wavebands compatible with the SeaWiFS ocean color satellite. The first is a modified Tethered Spectral Radiometer Buoy (TSRB-II) which simultaneously measures incident irradiance (Ed) and upwelling radiance (Lu) in 14 wavebands, including 4 in the UV (2 nm bandwidth). The second is a SeaWiFS Profiling Multichannel Radiometer (SPMR) which measures vertical profiles of downwelling irradiance in wavebands identical to the TSRB-II. Both instruments are deployed simultaneously to accumulate UV/VIS optical data (Ed, Lu, & Kd) while collecting discrete rosette samples at the same station. Each sample is evaluated for particulate absorption (including detrital correction), dissolved absorption (at least in the UV), and particulate pigments.

We use two laboratory irradiation strategies to quantify photochemical carbon mineralization (DIC & CO): (1) Full spectrum irradiations with a solar simulator (DSET Suntest CPS, Heureus) and/or natural sunlight that allows evaluation of the statistical uncertainties and upper bounds for mathematical predictions of photoproduction in different waters. (2) Narrow bandwidth monochromatic irradiations (normally using an Oriel 1/4 meter monochromator with 1000W Xe source) that establish wavelength-based quantum efficiencies (Φ) for photochemical and coincident physical/chemical (ex. fading) alterations of the CDOM. Photochemical production rates are compared to wavelength dependent extinction coefficients, irradiation history, bleaching rate, and environmental variables (pH, temperature, salinity, etc.). The combination of spectral photochemical efficiency data, absorbance data, irradiation profiles generated either using the SPMR or optical models, and measurements of solar spectral irradiance will allow predictions of whole column photoproduction.

Using relationships developed by deployments of the TSRB-II and SPMR, we plan to combine remotely-sensed data with irradiance and water optical models to estimate the photomineralization of CDOM in the coastal ocean (*à la.* J.J. Cullen et al., ASLO 1997). These data will represent the beginning of regional photochemical inventories and a starting point for long term regional scale studies of photochemical carbon transformations in the coastal ocean.

At Dalhousie, Sophie Johannessen (Ph.D. student) and W. Miller (PI) are involved in all components of this approach. Another graduate student (Lori Ziolkowski) and a technician (Penny Kuhn) have been added to the effort this year. Lori's background is in chemistry and Penny's is in optical modeling. Our field optical component benefits greatly from the participation of J.J. Cullen's group (w/ R. Davis, B. Nieke, also at Dalhousie) and assistance from Satlantic, Inc. (instrument development, optical expertise, field and computer assistance). We have collaborated with N. Blough's group at the University of Maryland (w/ A. Vodacek) by sharing shiptime and they have provided additional field optical data.

WORK COMPLETED

This year, a conductivity probe and tilt sensor were added to the SPMR and both were tested for compatibility and data quality during a cruise in the Atlantic Bight. These additions complete the planned instrument complement for the SPMR that we have assembled over the first three years of this

project. The current configuration includes 14 UV-VIS optical channels, a WETStar miniature fluorometer, tilt sensor, and instruments to provide conductivity, temperature, and pressure. The 1998 cruise resulted in 31 optical stations with an average of 3 replicate profiles each. This completes our field collaboration with Blough in the Atlantic Bight (four 7-day cruises, 118 stations, 3 seasons). We are currently comparing and compiling field and laboratory optical data for publication.

We have used a newly constructed irradiation box (15 long-pass filters over custom quartz containers) to allow quantum yield data to be generated more quickly than traditional monochromatic irradiation techniques. This system saw its first successful use at sea in the North Atlantic to examine the wavelength efficiency for carbon disulfide photoproduction (Xie et al., 1998). We also began experiments of CDOM fading and CO₂ photoproduction using the box to determine the wavelength dependent efficiencies for these processes.

New MATLAB® code has been developed to speed the analysis of both field and laboratory spectral data. We have successfully incorporated the methods of Rundel (1983) in our quantum efficiency calculations and improved procedures for calculating Kd and dark-correction in collaboration with M. Lewis and J.J. Cullen.

RESULTS

In accordance with our approaches listed above, we have continued to accumulate samples and optical data for diverse water types in an effort to build robust optical relationships that will be useful in predicting photochemistry from remotely sensed data. We have assembled optical instrumentation that gives excellent data for both *in situ* and reflected UV/VIS radiation (Ed, Lu, & Kd). We began evaluating the relationships present in field data between Lu and Ed in each waveband in the UV (typical result for the 323nm channel presented in Figure 1 below) and are evaluating similar extrapolation between Lu's in the visible and Kd's in the UV. We are currently examining methods to account for particle absorption in the UV using ratios for visible bands. Profile data has been used to calculate the *in situ* spectral slope of attenuation for comparison to CDOM spectra at the same stations (Miller et al., EOS, 1998).

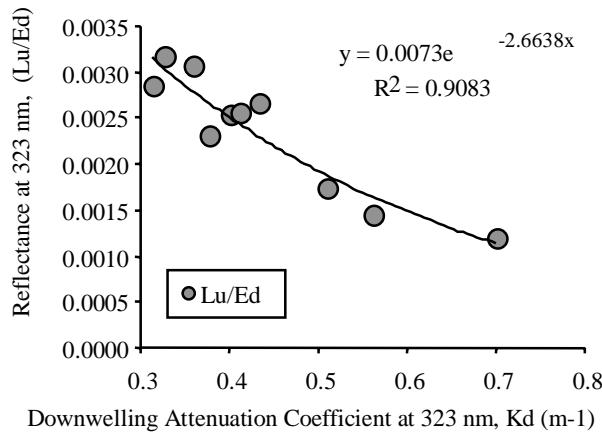


Figure 1. Relation between attenuation and reflected radiation at 323 nm, Bering Sea

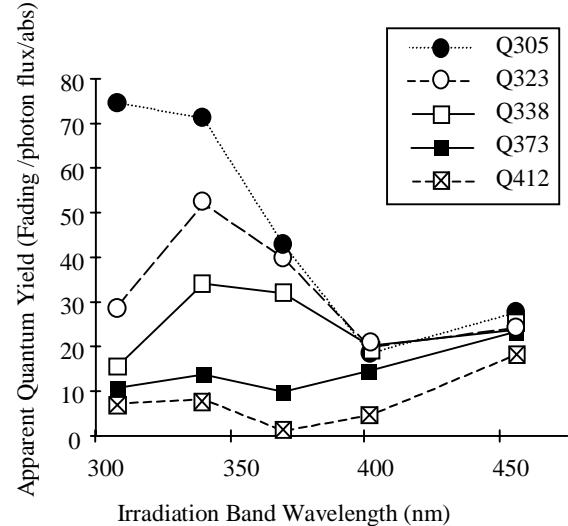


Figure 2. Spectral dependence for CDOM fading at SPMR wavelengths, N.W. Arm water

Data from some vertical optical profiles in the Atlantic Bight supported the presence of a photochemically faded water mass in the seasonal mixed layer. At these stations, an increase in UV attenuation was observed at the base of the mixed layer while an equivalent trend was not seen for visible wavelengths. Follow-up laboratory irradiations have provided data on the wavelength dependence of this CDOM fading process. These preliminary data from local waters (Figure 2 above) are presently being used to structure a mixed layer model that will provide a tool to examine the subtleties of CDOM spectral fading (particularly changes in spectral slope) in different water types.

IMPACT / APPLICATION

The optical properties of CDOM in the ocean control photochemical rates, effect oceanic chemical cycles, and influence the interpretation of ocean color (Miller, 1998a; 1998b). Based on data from the field, we feel that instrumentation capable of characterizing UV radiation in the surface ocean will prove invaluable to the understanding of the variability in the CDOM signal. While a large effort will be needed on both optical and photochemical research fronts, the approach developed thus far appears to be sound and should lead to novel and critical insight on the link between ocean optics and photochemical carbon transformations. It will also result in the unique ability to address the regional and global significance of photochemical reactions in the ocean.

TRANSITIONS

In addition to our main work in the Atlantic Bight, both instruments developed as part of this project have also been successfully deployed in the Gulf of St. Lawrence (B. Nieke, post. doc. w/ Cullen) the Bering Sea, and the Southern Ocean (Cullen). The TSRB-II (mounted in a modified frame for very shallow Lu deployment) has been deployed to study UV effects on coastal lakes (collaboration with J. Cullen, and T. Clair, Environment Canada). Based on the utility of the optical system we have assembled, we have received offers to participate with several groups interested in other photochemical processes. This should result in the opportunity to add varied water types to our expanding database.

Parts of the field data for the Atlantic Bight will be prepared for publication with N. Blough (Univ. Maryland, ONR funded). Planned development of MATLAB® algorithms for optical data base management (M. Lewis, Dalhousie Univ., ONR) will incorporate our field optical data as part of a searchable database.

RELATED PROJECTS

As stated above, we have collaborated with N. Blough (ONR) on fieldwork, sharing optical data and ship time. His efforts are on CDOM photochemistry.

We have a collaborated with M. Lewis (ONR), also at Dalhousie, in his study of bio-optical variability and development of novel optical instrumentation. J. Cullen works closely with both Dr. Lewis and myself on optical models, data analysis, and instrument development. The timely development of our novel Satlantic instruments depends heavily on these relationships.

During 1998 we conducted fieldwork for a project funded by the Canadian National Science and Engineering Council (NSERC) to study DOM photochemistry in an Arctic polynya. During 4 continuous months at sea we collected over 1000 discrete CDOM measurements from vertical profiles at about 40 stations. We will use these data to examine CDOM variability and its relation to *in situ* optics and reflectance data measured by others in the project. We are not funded for optical measurements in this project.

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